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DOW POLYURETHANES
Flexible Foams

Flexible Polyurethane Foams

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MOLDED FOAM

Automotive Seat Cushions

Most of the seating cushions used in automobiles today are made from either hot or HR-molded foam. A small percentage are cut from slabstock foam buns.^{5.115-5.117} The wide diversity and intricate shapes involved in this application lend themselves to successful molding of foam. With the appropriate selection of starting isocyanate and polyol and with selective use of additives it is possible to form flexible molded foams meeting widely differing product application specifications. Another advantage of molding foam is the foaming in place of reinforcements or otherwise producing foams with multiple zones of hardness.

In the typical molding operation, a mold is preheated and waxed with a mold-release agent. A predetermined amount of a foam system is poured into the mold, then the lid is closed and locked, and the ingredients foam into the shape of the mold. After the part is cured, it is stripped from the mold and the process can be repeated.^{5.118-5.124} Success at molding foam in a reduced pressure atmosphere has been reported.^{5.125-5.127}

Preheating of the molds is necessary for several reasons. The overall density of a molded part can be affected by mold surface temperature. If the surfaces are cold or at uneven temperatures, the heat from the exothermic reactions may dissipate unevenly and result in nonuniform skin density. Preheating also helps to complete the reactions at the outer skins and thus reduces the cure time. Warm mold surfaces are necessary to evaporate carrier solvents introduced during the mold-release application step.

Because molding is inherently a batch operation, commercial molding machines are designed for intermittent operation. Valves are arranged so that raw materials can be recirculated between shots to help ensure uniform composition in the dispensed mix. Throughput rates for molding machines are generally lower than those of slabstock machines. The actual output must be carefully sized to supply the necessary amount of material to the mold before the mixture begins to foam.

The two major molding techniques in the polyurethane industry are the hot-cure and the cold-cure (or HR) processes. The hot-cure molding process was commercially established over 30 years ago. Formulations for hot-molded foam are similar to that of conventional slabstock foam except for use of lightly ethylene-oxide-capped polyols and slightly different catalyst packages. Significant external heat is applied to the mold after filling in order to obtain sufficient surface cure of the foam to allow its early removal from the mold.

The cold-cure or HR molding process is derived from the original hot molding and is designed to utilize much less externally applied energy. To accomplish this, polyol manufacturers build a more reactive molecule so that the reactions proceed faster and less overall cure energy is needed; e.g.,

lower oven temperatures. The essential differences between hot and HR molding are summarized in Table 5.3. Detailed discussions of other processing and physical property differences are available.^{5,128-129}

Table 5.3 Hot-Cure and HR-Molding Technologies

	Hot-Cure	HR
Isocyanate	80/20 TDI	80/20 TDI Blends w/MDI Polymeric MDI MDI prepolymers
Polyol Molecular Weight EO-Capped Copolymer Polyol	2800-3500 Yes Optional	4500-6500 Yes Optional
Cure Oven Temperature	180-300°C 356-572°F	75--200°C 165-392°F
Postcuring	No	Optional
Mold Temperature at Pour	25-45°C 77-113°F	50-70°C 122-158°F

Foam Molding Lines

A typical foam molding line will consist of many functional parts. The larger portions of floor space will be taken up by conveying systems for the molds, ovens and related finished-foam handling systems. Conveyors for moving the foam molds from station to station can be of any number of layouts. Long racetrack-style designs are still as common as the newer, smaller and more specialized carousel lines like that shown in Figure 5.18. In most (but not all) cases, the mold moves under the mixing head to receive a charge of foam. It is common to find the mixing head mounted on a robot or other computerized pour bridge for purposes of optimizing pour pattern for each individual mold cavity. Technology has also been developed for using dedicated high-pressure mixing heads on stationary molds.

The molds are usually made of cast aluminum in two parts with provision for mechanically opening and closing the lid. For shorter production runs, sheet metal or sprayed metal tooling may be viable alternatives.^{5,130-5,131} Nonmetallic molds have also proven useful in less demanding applications.^{5,132-5,134} A critical comparison of alternative mold making materials is available.^{5,135}

For hot-cure foams, the molds are generally thin (6-10 mm) and lightly constructed. The lids are liberally drilled with holes to prevent air trapping and pressure buildup in the mold. HR and specialty molded foam molds are generally of heavier, more precise construction. The molds should be constructed to withstand up to 30 psig internal pressure. To build the pressure, the parting line seals should be made as tight as possible with



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Chapter 11

Molded Foams

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Since polyurethane foams expand and flow during the foaming reaction, many commercial products can be made by molding foam to size and shape in closed molds. It is estimated that 20 percent of total flexible foam production worldwide involves one of the molding techniques. Molded foams find application in all forms of transportation seating and trim parts, as well as in some upholstered furniture,^{11.1-11.2} bedding, packaging and novelty items.

Basically, foam molding involves pouring the reacting mixture into a suitable mold, closing the mold and allowing the foam to fill the mold. Details of the various foaming processes were discussed in Chapter 5. In addition to replicating the internal dimensions of the mold, the final product can also permanently record its part or style number and can incorporate physical inserts of various types. The typical methods of constructing a final automobile seat assembly have been reviewed.^{11.3}

If the mold is lined with a preformed plastic skin or textile fabric, dispersed foam will adhere to it and simplify the assembly requirements of many composite products. Technology for directly foaming onto a cover material preformed into a seat cushion mold has existed since 1955.^{11.4-11.7} Recent developments in vacuum-assisted foam-in-place technology for auto seating are discussed in References 11.8-11.19. Alternative schemes for bonding the cover fabric to the foam pad have been developed.^{11.20-11.24}

Closed molding is considerably more complicated than slabstock foam production. Factors which contribute to that complication include a higher reactivity formulation, pour-pattern limitations, the discrete size of each individual shot, the need to open and close a mold lid mechanically, the choice of release agent, mold temperature latitudes and the available curing cycle. Foam formulations used for molding and for slabstock differ mainly with respect to the catalyst packages and composition of the polyols. Generally, higher-molecular-weight, more reactive polyols are used for molding so that foams with good cure and rapid property development can be produced.

The two major molding techniques in the polyurethane industry today are the 'hot-cure' and the 'HR' or cold cure processes. As the name implies, hot-cure molding involves the application of high temperature to the mold during the cure cycle. This is necessary to drive the foam reaction to a sufficient degree of cure to permit the foam to be demolded in a timely manner and subjected to additional downstream fabrication steps. The newer HR foam molding process utilizes higher-reactivity ingredients so that less oven curing is needed.

Most molding is done in cast-aluminum molds, but there has been some use of reinforced-epoxy molds. Molds are usually made in two sections, with provision for mechanically opening and closing the lid.

For hot-molded foams, the lids contain many vent holes and generally "float" under restrained conditions. HR foam molds have less venting and must be constructed to withstand higher internal mold pressures. Heavier construction and tight seals are normally required. The importance of mold release cannot be overemphasized. Polyurethanes are excellent adhesives and will stick to bare metal. Molds are usually designed to allow about 1-2% shrinkage of the foam part after manufacture. It is best for the inner surface of the mold to have a mill run or other nonpolished surface to allow for good retention of the release agent. Additional mold construction details were discussed in Chapter 5. Nonmetallic molds have proven useful in molding furniture cushions.

SEATING FOAMS

In the area of transportation seating, flexible foams have become the material of choice not only because of the economies offered by large-scale molding operations but also because the cushioning and vibration damping characteristics of a foam can be easily adjusted to fit the requirements of the many different types of public and private transportation. Figure 11.1 illustrates the use of molded flexible foams in automotive seating applications.

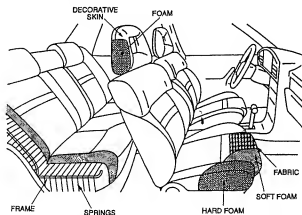
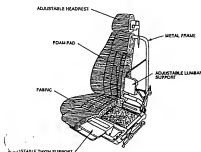


Figure 11.1 Typical Seating Applications for Flexible Foam

Worldwide, the older hot-molded foam technology is still in use. On the North American continent, the HR foam technology is dominant. One reason for that dominance, is a lower energy requirement. Figure 11.2 compares typical energy usage for alternative molding processes.

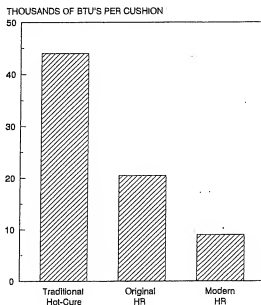


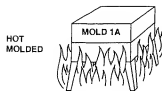
Figure 11.2
Energy Requirements of Molded Foam Processes
(Reconstructed from Reference 11.25)

HOT-MOLDED FOAMS

The most important application for hot-molded foam is as a contoured cushion laid atop tensioned springs in automotive seating. In general, formulations for hot-cure foams are based on nominal 3000-molecular weight ethylene-oxide-capped triols. Diols are often added for those applications requiring higher strength properties. For higher loads, it is common to blend in the filled or copolymer polyols discussed in Chapter 2. Alternatively, higher-functionality blended initiators have been used to produce higher-load-bearing foams. Typical hot-molded foam formulations are given in Table 11.1. If the foam is required to meet a flammability testing specification, a flame-retarding additive would be required.

Table 11.1 Typical Hot-Molded Foam Formulations

Component	Parts by Weight		
	Soft	Hard	Backrest
VORANOL CP-3111 Polyol	80	—	92
SPECIFLEX NH 104 Copolymer	20	100	—
SPECIFLEX NK 916 Additive	—	—	8
OSI RS 204	1.0	—	—
Tegostab B4900	—	0.8	1.0
NiMax A-1	0.10	0.04	0.08
Dabco 33-LV	—	0.10	0.08
Dabco XDM	0.40	—	0.13
Stannous Octoate	0.05	0.09	0.13
Water	2.4	2.1	3.5
VORANATE T-60 TDI Index	100	100	98



With the use of the SPECIFLEX NH-104 copolymer polyol and the SPECIFLEX NK-916 softening additive, the foam producer has the capability to make a wide range of both single and dual-hardness foams.^{11,26} The hot-molded foam process was discussed in Chapter 5. Mold temperature at pour is a critical variable. Optimum mold temperatures often fall in the range of 95-115°F (35-46°C). Lower temperatures result in a soft, densified foam core. When the mold gets too hot, the skin becomes loose and flaky, resulting in a poor overall cosmetic appearance. In the oven, sufficient heat must be applied to raise the temperature of the inner surface of the mold quickly up to about 250°F (120°C). This temperature approximates the exothermic reaction temperature of the interior of the foam, allowing sufficient cure for the foam to be demolded in 10 to 15 minutes. Cycling the molds down to the pour temperature and back up to the cure temperature is costly in terms of both energy and time.

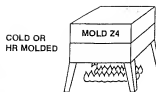
For more details of the hot-molding process and characteristics of the foams, see References 11.27-11.30. The most recent developments in hot-molded foam are discussed in References 11.31-11.36.

HR FOAMS

The term 'HR' is an abbreviation for the words 'high resiliency'. As it applies to foams, it refers to foams having dropping-ball-type resiliency test values significantly greater than those obtained with the conventional hot-molded or slabstock foams. One definition of HR foams requires that those foams possess a resiliency greater than 60%.^{11,37} Technology extending the achievable range of resiliency up to 70% has been reported.^{11,38} These foams have been referred to as the Extra-High-Resiliency (XHR) grade.

Today, the term HR foams is also generally taken to encompass the foams earlier referred to as cold-cure foam. HR molded foams offer several advantages:

1. Their support factor (ratio of 65% IFD to 25% IFD) is superior to that of conventional slab or hot-molded foams.
2. The amount of energy required to accelerate foam cure and develop final properties is less.
3. These foams can be formulated more easily to meet the requirements of various small-scale flammability tests.



An improvement in support factor means that a foam can offer higher load bearing at the use deflection and still maintain its soft initial feel. A typical HR foam shows a support factor around 2.2 to 3.0 or higher, while a conventional hot-cure foam has a support factor in the range of 1.7 to 2.0. Brown has described layered HR foam technology giving support factors as high as 5.0.^{11,3}

Some of the early history of HR molded foams in North America is recorded in References 11.39-11.40. The first HR foams appeared during the 1960s. These foams were based on ethylene-oxide-tipped polyether triols in combination with reactive diamine cross-linkers and various isocyanate compositions. Copolymer or grafted polyols were introduced for this application in the late sixties. Both technologies could produce foam meeting the various automotive specifications; but when the most popular diamine cross-linker was listed as a possible carcinogen in the early seventies, the copolymer polyol technology became dominant.

HR molded foams are typically made by the processes described in Chapter 5. HR foams are often made from specially formulated two-component systems. The base polyether triols used generally fall in the molecular-weight range of 4000 to 6000 and have 5 to 25% end capping with ethylene oxide to give primary hydroxyl contents ranging from about 65 to 90%.^{11.39} The comparative reactivity data presented in Figure 11.3 show that this variation in primary hydroxyl content is a fundamental way of designing the desired reactivity into a polyol (see Chapter 2 for a discussion of the test method).

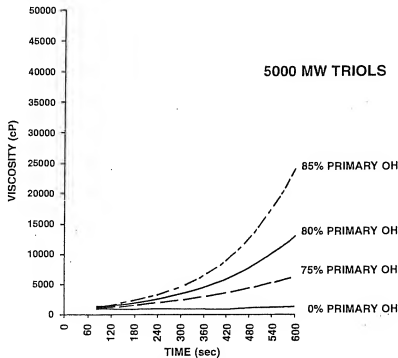


Figure 11.3
Comparative BVT Type Reactivity Data for
Polyols Used in Making HR Molded Foams

With more reactive polyols, the rate of gelation in HR foams is faster than in conventional foams. This translates into the need for less gelation catalyst than is used in slabstock and hot-molded foam. It also allows the use of (and, in some cases, the absolute need for) more blowing catalyst to accelerate the foam expansion reaction. The faster rate of polymer formation and the restricted expansion provided by the mold produces a foam containing a higher population of intact cell-walls when conventionally demolded. Because of this, and in contrast to hot-molded foam, HR foams must be crushed soon after demold to avoid shrinkage as the foam cools down. It is possible to formulate more or even perfectly open-celled foam, but such foams often border on instability, and most foam manufacturers choose to run tighter formulations. As long as the closed-cells can be adequately crushed open, it is safer to run a tight foam than to risk catastrophic foam instability.

Recent advances in HR polyol technology include higher functionality products for improved productivity^{11.42-11.43} and higher solids copolymer

polyols.^{11.44} Higher molecular weight polyols are reported to be helpful in attaining resiliency values over 70%.^{11.45} Liquid carbon dioxide has been successfully used to lower foam density in both TDI and MDI based formulations.^{11.46} Primary and secondary amine-capped-polyether polyols have also been used successfully to prepare a polyurea-type HR molded foam.^{11.47-11.50}

HR foams generally require less active silicone surfactants and in many cases require only cell-size-regulating types of surfactants. A typical low-density all-TDI based HR seating foam formulation is presented in Table 11.2.

Table 11.2 Typical Low-Density HR Seating Formulation

Component	Parts by Weight
SPECFLEX NC 630 Polyol	70
SPECFLEX NC 710 Copolymer	30
DC-5043	0.75
DC-5169	0.25
Diethanol Amine, pure	1.5
Dabco 33-LV	0.25
Niax A-1	0.08
Water	4.0
VORANATE T-80 TDI	100 Index

On a global basis, approximately 15% of all HR molded seating foam is made with a blend of TDI with one of the polymeric forms of MDI. A common ratio is 80 weight percent TDI, 20 weight percent polymeric MDI. A typical formulation for this grade of foam is presented in Table 11.3.

Table 11.3 Typical HR Seating Formulation Based On Blended TDI/PMDI Isocyanates

Component	Parts by Weight
SPECFLEX NC 630 Polyol	70
SPECFLEX NC 710 Copolymer	30
Tegostab B-4113	0.6
Tegostab B-8708	0.4
Dabco 33-LV	0.3
Niax A-1	0.1
Water	3.5
SPECFLEX TM-20 Isocyanate	100 Index

In traditional HR foam chemistry, the soft-segment portion of the foam matrix is a polymer containing urethane linkages resulting from the reaction of polyol with isocyanate. Polyurea structures result from the reaction of formulation water with isocyanate. For foams made from toluene diisocyanate and diethanol amine cross-linker (as in Table 11.2), it is

generally conceptualized that these reactions lead to a two-phase morphology consisting of discrete hard-segment domains dispersed within a continuous soft-segment polymer phase.^{11.51-11.52} An additional reinforcing phase may be present if the foam has been formulated to contain particulate fillers. Figure 11.4 offers a conceptual representation of such a system.

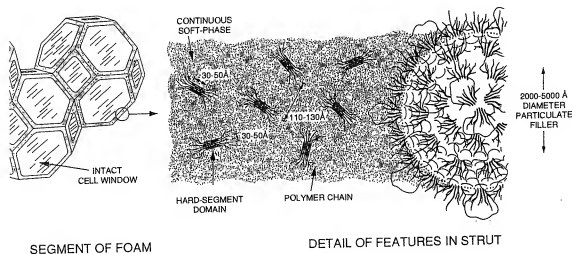


Figure 11.4 Conceptual Morphology of HR Foams

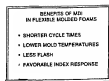
In the figure, the hard-segment domains are represented by the clustered straight lines. Our best estimates of physical dimensions for these structures are indicated.^{11.53} These features are tied into the matrix by covalent attachment to or entanglement with polymer chains (the wiggly lines) that are shown fading off into the continuous soft-segment phase. A size range for traditional styrene/acrylonitrile type copolymer polyol filler particles is also given.

Prior to discussing general seating foams in more detail, three special classes of foam receiving notable recent attention will be discussed below.

ALL-MDI FOAM

Commercially useful seating foams can be made from either TDI or MDI-based technology. The competition between the two technologies began early and continues today.^{11.54-11.64} An excellent comparison of the two foam types has been presented.^{11.65}

Some of the advantages of MDI-based systems are: shorter production cycles, utilization of lower mold temperatures, reduction in waste foam from mold vents and seals, and the higher inherent rate of foam cure. MDI-based foams cure so quickly that traditional forms of auxiliary curing heat are often not needed. The higher rate of cure reduces the time a given shot of foam must remain in the mold before it can be demolded and sent for further fabrication. Demold times of as little as ninety seconds have been observed. Quality



checks can be performed sooner, and it is not uncommon for MDI-based foam pads to be fabricated into covers and shipped within a few hours. All this increases production capabilities and reduces the need for large inventories of foam pads at various stages of cure.

MDI-based foams can be made on any of the molded foam production equipment described in Chapter 5. Two component systems are generally used with both sides specially formulated for the intended application. The base polyols used are blends of ethylene-oxide-capped triols and diols. Triols in the molecular-weight range of 4000 to 7000 are the most useful. Typical diols range from 2000 to 4000-molecular-weight. The isocyanate side is frequently a blend of a polymeric MDI with a prepolymer or with the pure 2,4' or 4,4' MDI isomers. A typical starting formulation is presented in Table 11.4.

Table 11.4 Typical All-MDI Based HR Foam Formulation

Component	Parts by Weight
VORANOL CP 4711 Polyol	98.0
VORANOL CP 5021 Polyol	2.0
Tegostab B-4113	1.0
Diethanol Amine, 85%	0.8
Dabco 33-LV	0.55
Niax A-1	0.1
Water	3.4
SPECIFLEX NE-106 Isocyanate, Index	80-110

Fast viscosity increase is a characteristic of MDI-based systems that often leads to in-mold flowability problems. Accurate temperature control of the process streams is helpful in minimizing flowability problems. Functionality and pure isomer content are the main chemical variables that affect foam flowability. The low free NCO content of MDI-based isocyanates compared to TDI, results in a reduced blowing efficiency. Figure 11.5 illustrates the typical density differences seen when the same amount of water is used in each type of foam.

Efforts to reduce the blowing deficiency with few catalysts and surfactants have been reported.^{11,66-11,67} Further density reduction efforts should be aided by use of the new liquid carbon dioxide auxiliary blowing agent technology.^{11,68}

Another useful feature of MDI-based foams is their strong response to widely varying isocyanate index. Figure 11.6 compares the typical index response of TDI-based foam systems to that for MDI-based systems.

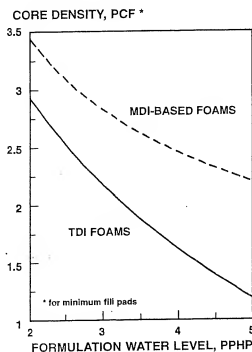


Figure 11.5 Typical Density Differences in All-Water Blown Foams

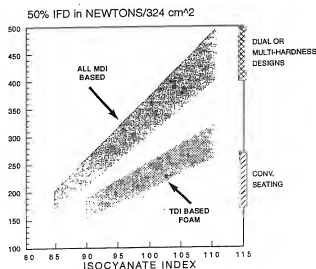


Figure 11.6 Typical Index Response in Foams Made with TDI and MDI Type Isocyanates

Clearly, a given MDI-based system has a greater capability than a TDI-based system to satisfy a wide range of customer load-bearing specifications. Reference 11.69 details how this strong index response can have serious negative effects on other important foam properties. References 11.70-11.74 discuss the utilization of MDI's favorable load-to-index response for the preparation of dual-hardness foams.

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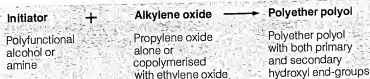
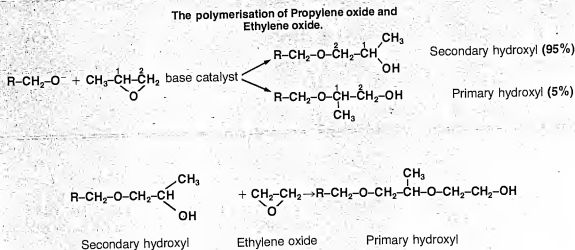


Figure 3-16 The manufacture of polyether polyols.



Polyether polyols

About 90% of the polyols used in polyurethane manufacture are hydroxyl-terminated polyethers. These are made by the addition of alkyene oxides, usually propylene oxide, onto alcohols or amines which are usually called starters or 'initiators'. The addition polymerisation of propylene oxide occurs with either anionic (basic) and cationic (acidic) catalysis although commercial polyol production is usually by base catalysis. The epoxide ring of propylene oxide may theoretically open at either of two positions on reaction but, in practice, the ring opens preferentially at the less sterically-hindered position with base catalysis. Polyethers based on propylene oxide thus contain predominantly secondary hydroxyl end-groups. Secondary hydroxyl end-groups are several times less reactive with isocyanates than primary hydroxyl groups and for some applications polyether polyols based only on propylene oxide may have inconveniently low reactivity.

The primary hydroxyl content may be increased by the separate reaction of the polyoxypropylene polyols with ethylene oxide to form a block copolymer with an oxyethylene 'tip'. By this means the primary hydroxyl end-group content may be varied from about 5% to over 80% of the total hydroxyl end-groups.

Polyether polyols for flexible polyurethanes. Most of the polyether polyols used to make flexible polyurethane foams and elastomers are triols based on trifunctional initiators, mainly glycerol or trimethylolpropane. Polyether diols, made using glycol initiators, are also frequently used, often together with triols, in making high-elongation foams and elastomers. These high molecular weight polyether polyols are made mainly from propylene oxide but are usually modified by the co-polymerisation of 5% to 20% of ethylene oxide.

The many polyether polyols used to make flexible polyurethanes include speciality products for the production of flat-top slabstock foam, polyether polyols for moulded flexible and semi-rigid foams, and specially developed polyethers for elastomers, RIM products, adhesives and coatings.

The majority of flexible foam is made from 80:20-TDI and polyether triols with molecular weights in the range from 3,000 to 4,000. A typical triol with a mean molecular weight of 3500 is made by the addition polymerisation of 50 to 55 moles of propylene oxide and 10 to 15 moles of ethylene oxide onto 1 mole of glycerol or trimethylolpropane. Both the quantity and the position of the oxyethylene groups in the polyoxypropylene chains are important when tailoring the polyether polyol system for use in a particular process for making slabstock or moulded foam, and in obtaining a foam rise that is sufficiently robust to be unaffected by minor variations in processing conditions.

A side reaction in the base catalysed polymerisation of propylene oxide produces unsaturated end-groups that do not react with isocyanates. Polyol manufacturers control this reaction and limit the unsaturation of their products. One effect of unsaturated end-group formation is to reduce the effective functionality of the polyol, but, in practice, this is significant only for polyols with equivalent weights above about 1300.

The epoxide monomers and the polyether polyols are easily oxidised. Air is excluded from the manufacturing process and, when polymerisation is complete, antioxidants are added to prevent oxidation of the polyether. Much work has been done to develop efficient antioxidant systems. Many polyether polyols contain a synergistic mixture of antioxidants that not only protect the polyol from oxidation during storage, but also protect low density foam from oxidative scorch at the high curing temperature immediately after manufacture.

Modified polyether polyols. There are three main types:

- 1) Polyvinyl-modified polyethers or 'polymer polyols'.
- 2) Polyols containing polyurea dispersions (PHD polyols (Poly Harnstoff Dispersion)).
- 3) Polyols containing polyurethane dispersions (PIPA polyols (PolyIsocyanate Poly Addition)).